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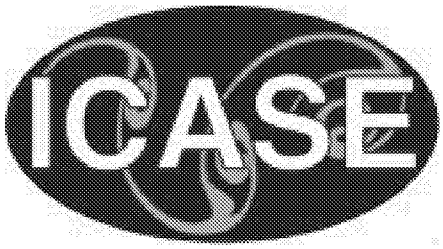

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THEORY OF THE LATTICE BOLTZMANN METHOD: LATTICE BOLTZMANN MODELS FOR NON-IDEAL GASES

LI-SHI LUO*

Abstract. In this paper a procedure for systematic *a priori* derivation of the lattice Boltzmann models for non-ideal gases from the Enskog equation (the modified Boltzmann equation for dense gases) is presented. This treatment provides a unified theory of lattice Boltzmann models for non-ideal gases. The lattice Boltzmann equation is systematically obtained by discretizing the Enskog equation in phase space and time. The lattice Boltzmann model derived in this paper is thermodynamically consistent up to the order of discretization error. Existing lattice Boltzmann models for non-ideal gases are analyzed and compared in detail. Evaluation of these models are made in light of the general procedure to construct the lattice Boltzmann model for non-ideal gases presented in this work.

Key words. kinetic method, Enskog theory, non-ideal gases, lattice Boltzmann equation

Subject classification. Fluid Mechanics

1. Introduction. In recent years, there has been significant progress made in the development of the lattice Boltzmann equation (LBE) method [48, 29, 28, 6, 10, 1, 38], a novel technique developed for modeling various complex systems, especially complex fluids. One particular application of the lattice Boltzmann method which has attracted considerable attention is the modeling of inhomogeneous fluids, such as non-ideal gases or multi-component fluids [21, 18, 19, 20, 59, 59, 61, 62, 51, 50, 27, 46]. These flows are important, but are difficult to simulate by conventional techniques for solving the Navier-Stokes equations. The main difficulty conventional techniques face is due to the interfaces in inhomogeneous flow. Computationally, one might be able to track a few, but certainly not very many interfaces in a system. It is therefore impractical to simulate a realistic system, which is inhomogeneous in density or composition, by directly solving the Navier-Stokes equations without making some drastic approximations. One can also view this problem from a different perspective: Interfaces between different components or phases of a fluid system are thermodynamic effects resulting from interactions among molecules. To solve the Navier-Stokes equations, one needs to know the equation of state, which is usually unknown in the interfacial regions. It is therefore difficult to incorporate thermodynamics into the Navier-Stokes equations in a consistent fashion, although the interfaces are precisely the result due to thermodynamical effects. Hence one encounters some fundamental difficulties.

There exists ample evidence that models based on the lattice Boltzmann equation, and its predecessor, the lattice-gas automata (LGA) [14, 65, 15], and other gas kinetic models [53, 68, 37], are particularly suitable for complex systems such as non-ideal gases and multi-component fluids [59, 60, 61, 62, 51, 50, 27]. There may be profound reasons for the success of the LGA and LBE models in simulating those complex systems. The LGA and LBE models do not start at the macroscopic level; instead, they start at mesoscopic level at which one can use a "*potential*" to model interactions in the system. Macroscopic or hydrodynamic behaviors of the system naturally emerge from mesoscopic dynamics, provided that the mesoscopic dynamics possesses the

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necessary and correct conservation laws with associated symmetries such as rotational invariance, Galilean invariance, *etc.* It is well known that the macroscopic behavior of a hydrodynamic system is rather insensitive to the microscopic or mesoscopic details — the details of microscopic or mesoscopic dynamics only affect the numerical values of the transport coefficients. This observation is a key physical insight in the construction of simplistic kinetic models such as the lattice gas automata and the lattice Boltzmann equation.

Historically, the lattice Boltzmann equation was first developed empirically [48, 29, 28, 6] from its predecessor — the lattice-gas automata [14, 65, 15]. This empiricism influences even the most recent lattice Boltzmann models [59, 60, 62, 61, 51, 50, 27]. Empirical lattice Boltzmann models usually have some inherent artifacts which are not yet fully understood. One particular problem with non-ideal gases or multi-component lattice Boltzmann models is the thermodynamic inconsistency: The so-called "equilibrium state" in these models cannot be described by thermodynamics. In particular, one has difficulties in defining an entropy of the system systematically, and thus leading to, for instance, the inconsistency between the thermodynamic pressure and the kinetic one [9]. Although this issue has been previously mentioned [62, 61], no progress has been made in solving this problem, despite its paramount importance.

It is well understood that the original Boltzmann equation only describes rarefied gases; it does not describe dense gases or liquids. In the Boltzmann gas limit (BGL), $N \to \infty$, $m \to 0$, and $r_0 \to 0$, $Nm \to$ finite, $Nr_0^2 \to$ finite, and $Nr_0^3 \to 0$, where N, m, and r_0 are the particle number, particle mass, and interaction range, respectively. Thus, in the BGL, the mean free path $l \sim 1/Nr_0^2$ remains constant, while the total interaction volume Nr_0^3 goes to zero. Therefore, in the strict thermodynamic sense, the Boltzmann equation only retains the thermodynamic properties of a *perfect* gas — there is no contribution to the transport of molecular properties from inter-particle forces, although collisions influenced by interparticle interaction are considered. In order to properly describe non-ideal dense gases, the effect of finite particle size, for instance, must be explicitly considered. It was Enskog who first extended the Boltzmann equation to dense gases by including the volume exclusion effect along the rationale of van der Waals theory [5], which leads to a non-ideal gas equation of state. The Enskog equation (the modified Boltzmann equation for dense gases) can indeed describe dense gases or liquids with non-ideal gas equation of state to certain extend. The Enskog equation describes a system consisting of hard spheres and it has been shown that the hard-sphere system captures most qualitative properties of a simple liquid [22, 57]. Furthermore, the revised Enskog theory seems to be valid for a wide range of density covering gas, liquid, and even solid [12].

It has been recently demonstrated [25, 26] that the lattice Boltzmann equation can be directly derived from the continuous Boltzmann equation. The method proposed in Refs. [25, 26] is a general procedure to construct the lattice Boltzmann models in a systematic and *a priori* fashion. Through this procedure we can better understand the approximation made in the lattice Boltzmann equation. The method also provides a means to analyze the existing lattice Boltzmann models. In this paper, the method of Refs. [25, 26] is applied to obtain the lattice Boltzmann equation for non-ideal gases (which have non-ideal gas equation of state). The lattice Boltzmann equation for non-ideal gases is derived from the Enskog equation for dense gases. The obtained lattice Boltzmann model for isothermal non-ideal gases has thermodynamic consistency in the sense of approximation, *i.e.*, it is only correct up to the order of discretization. In comparing all existing models, we would like to stress the fact that many defects of the existing LBE models are due to errors made at the level of fundamental concepts, rather than at the level of numerical implementation.

This paper is a detailed extension of a work previously published [43], and is organize as follows. In Sec. 2 the Enskog equation for dense gases with BGK approximation is briefly discussed. In Sec. 3 the discretization procedure to obtain the lattice Boltzmann equation for non-ideal gases from the Enskog equation is described.

The discretization in time and phase space, small velocity expansion of the equilibrium distribution, and realization of the forcing term in the lattice Boltzmann equation are also discussed in detail. In Sec. 4 the hydrodynamics and some related thermodynamical quantities of the model are given. In Sec. 5 the model derived in this work is compared with other existing lattice Boltzmann models for non-ideal gases, and the similarities and differences among the existing models are explicitly shown. Sec. 6 concludes the paper. A more detailed discussion on the Enskog equation for dense gases and derivation of the collision term leading to non-ideal gas equation of state are provided in Appendix A. The Chapman-Enskog analysis for the lattice Boltzmann model for non-ideal gases is demonstrated in Appendix B. In Appendix C, the forcing term in the Boltzmann equation is directly derived from an equilibrium distribution function shifted by the acceleration due to an external field. This derivation provides a simple and clear derivation of the models utilizing the external force to mimic the non-ideal gas effect.

2. Enskog Equation for Dense Gases. The Enskog equation [5, 30, 23] *explicitly* includes the radius of colliding particles, r_0, in the collision integral:

$$\partial_t f + \boldsymbol{\xi}\cdot\nabla f + \boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f = J\,, \tag{2.1a}$$

$$J = \int d\boldsymbol{\mu}_1 \left[g(\boldsymbol{x}+r_0\hat{\boldsymbol{r}}) f(\boldsymbol{x},\boldsymbol{\xi}') f(\boldsymbol{x}+2r_0\hat{\boldsymbol{r}},\boldsymbol{\xi}_1') - g(\boldsymbol{x}-r_0\hat{\boldsymbol{r}}) f(\boldsymbol{x},\boldsymbol{\xi}) f(\boldsymbol{x}-2r_0\hat{\boldsymbol{r}},\boldsymbol{\xi}_1) \right]\,, \tag{2.1b}$$

where f is the single particle (mass) distribution function, $\boldsymbol{\xi}$ and $\boldsymbol{a}$ are particle velocity and acceleration, g is the radial distribution function, $\hat{\boldsymbol{r}}$ is the unit vector in the direction from the center of the second particle of $f(\boldsymbol{x},\boldsymbol{\xi}_1)$ to the center of the first particle of $f(\boldsymbol{x},\boldsymbol{\xi})$ at the instant of contact during a collision, and $\boldsymbol{\mu}_1$ is the collisional space of the second particle of $f(\boldsymbol{x},\boldsymbol{\xi}_1)$. If we expand the collision operator J in a Taylor series about $\boldsymbol{x}$, use the BGK approximation [2, 23, 63, 40], and assume the fluid to be isothermal and incompressible, we obtain the following equation (details refer to Appendix A):

$$\partial_t f + \boldsymbol{\xi}\cdot\nabla f + \boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f = -\frac{g}{\lambda}[f - f^{(0)}] + J'\,, \tag{2.2a}$$

$$J' = -f^{(0)}\, b\rho\, g\, (\boldsymbol{\xi}-\boldsymbol{u})\cdot\nabla \ln(\rho^2 g)\,, \tag{2.2b}$$

where λ is the relaxation time which characterizes a typical collision process, and $f^{(0)}$ is the Maxwell local equilibrium distribution function [47] given by

$$f^{(0)}(\rho,\boldsymbol{u},\theta) = \frac{1}{z}\rho_0 (2\pi\theta)^{-D/2} \exp\left[-(\boldsymbol{\xi}-\boldsymbol{u})^2/2\theta - U(\boldsymbol{x})/\theta\right]\,, \tag{2.3}$$

where D is the dimension of the momentum space $\boldsymbol{\xi}$; ρ, $\boldsymbol{u}$, and $\theta = k_B T/m$ are mass density, macroscopic velocity, and the normalized temperature, respectively; k_B, T, and m are the Boltzmann constant, temperature, and molecular mass, respectively; $U(\boldsymbol{x})$ is a mean-field external potential (per unit mass),

$$\rho_0 = \frac{1}{V}\int d\boldsymbol{x} d\boldsymbol{\xi}\, f^{(0)} \tag{2.4}$$

is the average mass density in the system of volume V, and

$$z(\theta) \equiv \frac{1}{V}\int_V d\boldsymbol{x}\, \exp[-U(\boldsymbol{x})/\theta]\,. \tag{2.5}$$

The additional collision term, J' in Eqs. (2.2), includes the volume exclusion effect (see Appendix A for details). In the original work of Enskog, $g = g(b\rho)$, and b is the second virial coefficient in the virial

expansion of the equation of state for the hard-sphere system [5]. The hydrodynamic moments, *i.e.*, mass density ρ, velocity $\boldsymbol{u}$, normalized temperature θ, and energy density e can be defined as follows:

$$\rho = \int d\boldsymbol{\xi} f^{(0)} = \int d\boldsymbol{\xi} f = \frac{1}{z}\rho_0 \exp(-U/\theta)\,, \tag{2.6a}$$

$$\rho \boldsymbol{u} = \int d\boldsymbol{\xi}\boldsymbol{\xi} f^{(0)} = \int d\boldsymbol{\xi}\boldsymbol{\xi} f\,, \tag{2.6b}$$

$$\frac{D}{2}\rho\theta = \int d\boldsymbol{\xi}\, \frac{1}{2}(\boldsymbol{\xi}-\boldsymbol{u})^2 f^{(0)} = \int d\boldsymbol{\xi}\, \frac{1}{2}(\boldsymbol{\xi}-\boldsymbol{u})^2 f\,, \tag{2.6c}$$

$$\rho e = \int d\boldsymbol{\xi}\, \left[\frac{1}{2}(\boldsymbol{\xi}-\boldsymbol{u})^2 + U(\boldsymbol{x})\right] f^{(0)} = \int d\boldsymbol{\xi}\, \left[\frac{1}{2}(\boldsymbol{\xi}-\boldsymbol{u})^2 + U(\boldsymbol{x})\right] f\,. \tag{2.6d}$$

The acceleration $\boldsymbol{a}$ is purely due to an external field, $U(\boldsymbol{x})$, *i.e.*,

$$\boldsymbol{a} \equiv \dot{\boldsymbol{\xi}} = -\nabla U\,. \tag{2.7}$$

For the Enskog equation or the revised Enskog equation, both global [56] and local [44, 45, 52] H-theorem can be proved.

To emphasize that the acceleration $\boldsymbol{a}$ is strictly due to an external field or its equivalent, the derivation of the Boltzmann equation *via* the BBGKY hierarchy is briefly reviewed in the following. Given a Hamiltonian system of N particles, the N-particle distribution function $f_N(\boldsymbol{x}^{(N)}, \boldsymbol{\xi}^{(N)}, t)$ satisfies the following Liouville equation:

$$\partial_t f_N + \sum_{i=1}^{N} \left(\boldsymbol{\xi}_i\cdot\nabla_i + \dot{\boldsymbol{\xi}}_i\cdot\nabla_{\boldsymbol{\xi}_i}\right) f_N = 0, \tag{2.8}$$

where $\nabla_i \equiv \nabla_{\boldsymbol{x}_i}$, $\boldsymbol{x}^{(N)} \equiv \{\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N\}$ (similar for $\boldsymbol{\xi}^{(N)}$), and

$$\dot{\boldsymbol{\xi}}_i = \boldsymbol{a}_i - \sum_{j\neq i} \nabla_j V(\|\boldsymbol{x}_i - \boldsymbol{x}_j\|) = -\nabla_i U - \sum_{j\neq i} \nabla_j V_{ij}\,, \tag{2.9}$$

and $\boldsymbol{a}_i = -\nabla_i U$ is the acceleration due to external force (one-body interaction U), and $V_{ij} \equiv V(\|\boldsymbol{x}_i - \boldsymbol{x}_j\|)$ is the two-body interaction potential among the particles ($V_{ii} = 0$). By distinguishing the external field and interparticle interactions, the Liouville equation can be rewritten as the following:

$$\partial_t f_N + \sum_{i=1}^{N} \left(\boldsymbol{\xi}_i\cdot\nabla_i + \boldsymbol{a}_i\cdot\nabla_{\boldsymbol{\xi}_i}\right) f_N = \sum_{i=1}^{N}\sum_{j\neq i} \nabla_j V_{ij}\cdot\nabla_{\boldsymbol{\xi}_i} f_N\,. \tag{2.10}$$

The reduced distribution function, f_M for $1 \leq M < N$,

$$f_M \equiv \int d\boldsymbol{x}^{(N-M)} d\boldsymbol{\xi}^{(N-M)}\, f_N\,,$$

where $\boldsymbol{x}^{(N-M)} \equiv \{\boldsymbol{x}_{N-M+1}, \boldsymbol{x}_{N-M+2}, \ldots, \boldsymbol{x}_N\}$ (and similar for $\boldsymbol{\xi}^{(N-M)}$), satisfies the following equation [22, 23]:

$$\partial_t f_M + \sum_{i=1}^{M} \left(\boldsymbol{\xi}_i\cdot\nabla_i + \boldsymbol{a}_i\cdot\nabla_{\boldsymbol{\xi}_i}\right) f_M = (N-M)\sum_{i=1}^{M} \int d\boldsymbol{x}_{M+1} d\boldsymbol{\xi}_{M+1} \nabla_{M+1} V_{i,M+1}\cdot\nabla_{\boldsymbol{\xi}_i} f_{M+1}\,, \tag{2.11}$$

The above equation is the celebrated BBGKY hierarchy. The first equation in the hierarchy for the single particle distribution function $f(\boldsymbol{x}, \boldsymbol{\xi}, t) \equiv f_1(\boldsymbol{x}_1, \boldsymbol{\xi}_1, t)$ is:

$$\partial_t f + \boldsymbol{\xi}\cdot\nabla f + \boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f = (N-1)\int d\boldsymbol{x}_2 d\boldsymbol{\xi}_2\, \nabla_2 V_{12}\cdot\nabla_{\boldsymbol{\xi}} f_2(\boldsymbol{x}, \boldsymbol{\xi}, \boldsymbol{x}_2, \boldsymbol{\xi}_2, t)\,, \tag{2.12}$$

where $\boldsymbol{a} \equiv \boldsymbol{a}_1 = -\nabla_1 U$ is purely an effect due to the external field U. The two-particle distribution function f_2 can be decomposed symbolically as the following:

$$f_2(\boldsymbol{x}_1, \boldsymbol{\xi}_1, \boldsymbol{x}_2, \boldsymbol{\xi}_2, t) = C_2(\boldsymbol{x}_1, \boldsymbol{x}_2, t) f(\boldsymbol{x}_1, \boldsymbol{\xi}_1, t) f(\boldsymbol{x}_2, \boldsymbol{\xi}_2, t)\,, \tag{2.13}$$

where $C_2(\boldsymbol{x}_1, \boldsymbol{x}_2, t)$ is a pair correlation function [23, 35]. Depending on the approximation applied to the pair correlation $C_2(\boldsymbol{x}_1, \boldsymbol{x}_2, t)$, different closure would result from the kinetic equation (2.12) [23, 35]. For example, with the approximation that either $g_2 = 1$, *i.e.*,

$$f_2(\boldsymbol{x}_1, \boldsymbol{\xi}_1, \boldsymbol{x}_2, \boldsymbol{\xi}_2, t) = f(\boldsymbol{x}_1, \boldsymbol{\xi}_1, t) f(\boldsymbol{x}_2, \boldsymbol{\xi}_2, t)\,,$$

or $C_2(\boldsymbol{x}_1, \boldsymbol{x}_2, t) = g(\|\boldsymbol{x}_1 - \boldsymbol{x}_2\|)$, where g is the radius distribution function for the hard sphere system, *i.e.*,

$$f_2(\boldsymbol{x}_1, \boldsymbol{\xi}_1, \boldsymbol{x}_2, \boldsymbol{\xi}_2, t) = g(\|\boldsymbol{x}_1 - \boldsymbol{x}_2\|) f(\boldsymbol{x}_1, \boldsymbol{\xi}_1, t) f(\boldsymbol{x}_2, \boldsymbol{\xi}_2, t)\,,$$

the first equation of the BBGKY hierarchy, Eq. (2.12), leads to either the Boltzmann equation or the Enskog equation, respectively [23, 35].

It is apparent that the acceleration $\boldsymbol{a}$ is due to a self-consistent external field which is one-body interaction in nature, as clearly and explicitly illustrated in the derivation of the Boltzmann equation from Liouville equation *via* BBGKY hierarchy [23, 30, 35, 36, 40]. In other words, the potential U in the Maxwellian defined by Eq. (2.3) only represents an external field of body-force type, and this self-consistent mean-field interaction should not be confused with genuine multi-body interactions which take place in non-ideal gases. In the Boltzmann equation, all the interactions among particles (multi-body interactions) involved in a collision process are considered in the collision operator, represented by collision cross section. In particular, the collision operator reduces to a parameter λ of the single relaxation time in the case of the BGK equation. In the limit of BGL, the interactions among particles have no effect other than changing the numerical value of the viscosity, as clearly illustrated by the BGK model. Therefore, non-ideal gas effects are not included in the Boltzmann equation. To exhibit non-ideal gas effects in the thermodynamical limit, the finite range of the interactions among particles in the same limit (the finite size effect or the volume exclusion effect), which causes non-ideal gas effects, must be explicitly considered. As is shown in detail later in Sec. 5, the existing LBE models use some form of one-body interaction to mimic non-ideal gas effects. While this approximation of multi-particle interaction by a mean-field one-body interaction seems to allow LBE models to simulate isothermal non-ideal gases because the effect of pressure and forcing can be distinguishable in the momentum equation. However, this is no longer true in the energy equation. Pressure and forcing act quite differently in the energy equation: the former affects the energy transport as $P\nabla \cdot \boldsymbol{u}$ whereas the latter does work as $\rho \boldsymbol{a} \cdot \boldsymbol{u}$. In addition, the multi-particle interactions affect the heat conductivity whereas the forcing does not. This suggests some inevitable adverse consequences of the approximation. The only way to correctly model non-ideal gases is to at least include the "finite size effect" explicitly. And the Enskog equation is one such model.

A formal solution of the Enskog equation with BGK approximation, Eq. (2.2), can be obtained by integrating along characteristic line $\boldsymbol{\xi}$ over a time interval of length δ_t [36]:

$$\begin{aligned} f(\boldsymbol{x} + \boldsymbol{\xi}\delta_t + \frac{1}{2}\boldsymbol{a}\delta_t^2, \boldsymbol{\xi} + \boldsymbol{a}\delta_t, t + \delta_t) &= e^{-\delta_t g/\lambda} f(\boldsymbol{x}, \boldsymbol{\xi}, t) + \frac{g}{\lambda} e^{-\delta_t g/\lambda} \int_0^{\delta_t} e^{t' g/\lambda} f^{(0)}(\boldsymbol{x}(t'), \boldsymbol{\xi} + \boldsymbol{a}t', t + t')\, dt' \\ &+ e^{-\delta_t g/\lambda} \int_0^{\delta_t} e^{t' g/\lambda} J'(\boldsymbol{x}(t'), \boldsymbol{\xi} + \boldsymbol{a}t', t + t')\, dt' - e^{-\delta_t g/\lambda} \boldsymbol{a} \cdot \int_0^{\delta_t} e^{t' g/\lambda} \nabla_{\boldsymbol{\xi}} f(\boldsymbol{x}(t'), \boldsymbol{\xi} + \boldsymbol{a}t', t + t')\, dt'\,, \end{aligned} \tag{2.14}$$

where $\boldsymbol{x}(t') = \boldsymbol{x}(t) + \boldsymbol{\xi}t' + \frac{1}{2}\boldsymbol{a}t'^2$ is the (approximated) trajectory under the influence of the external field.[1]

[1] We neglected the term of t'^2 in [43] because it does not affect the final result.

The approximation is made by the assumption that the acceleration $\boldsymbol{a}$ is a constant locally. Note that the above equation is implicit because of not only the term $\nabla_{\boldsymbol{\xi}} f$, but also the time-dependence of hydrodynamic moments ρ, $\boldsymbol{u}$, and θ in the equilibrium $f^{(0)}$, and J'.

Our derivation of the lattice Boltzmann equation is based upon the discretization of the above integral solution of the Enskog equation. In what follows, we show that the lattice Boltzmann equation is an explicit finite difference scheme for solving the above integral solution of the Enskog equation.

3. Derivation of Lattice Boltzmann Equation.

3.1. Discretization in time. By using the mean-value theorem, we can rewrite the integral solution of the BGK Enskog equation, Eq. (2.14), as follows:

$$\begin{aligned} f(\boldsymbol{x}+\boldsymbol{\xi}\delta_t+\frac{1}{2}\boldsymbol{a}\delta_t^2,\,\boldsymbol{\xi}+\boldsymbol{a}\delta_t,\,t+\delta_t) &= e^{-\delta_t g/\lambda}\, f(\boldsymbol{x},\,\boldsymbol{\xi},\,t)+\frac{1}{\lambda}e^{-\delta_t(1-\epsilon)g/\lambda} f^{(0)}(\boldsymbol{x}(\epsilon\delta_t),\,\boldsymbol{\xi}+\boldsymbol{a}\epsilon\delta_t,\,t+\epsilon\delta_t)\,\delta_t \\ &+e^{-\delta_t(1-\epsilon)g/\lambda} J'(\boldsymbol{x}(\epsilon\delta_t),\,\boldsymbol{\xi}+\boldsymbol{a}\epsilon\delta_t,\,t+\epsilon\delta_t)\,\delta_t - e^{-\delta_t(1-\epsilon)g/\lambda}\boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f(\boldsymbol{x}(\epsilon\delta_t),\,\boldsymbol{\xi}+\boldsymbol{a}\epsilon\delta_t,\,t+\epsilon\delta_t)\,\delta_t\,, \end{aligned} \tag{3.1}$$

where ϵ is a constant between 0 and 1, and $\boldsymbol{x}(\epsilon\delta_t) \equiv \boldsymbol{x}(t)+\boldsymbol{\xi}\epsilon\delta_t+\frac{1}{2}\boldsymbol{a}(\epsilon\delta_t)^2$. If we assume that δ_t is small enough and $f^{(0)}$, J', and $\nabla_{\boldsymbol{\xi}} f$ are smooth enough locally in phase space, we can neglect the terms of the order $O(\delta_t^2)$ or smaller in the Taylor expansion of Eq. (3.1), and obtain

$$f(\boldsymbol{x}+\boldsymbol{\xi}\delta_t,\,\boldsymbol{\xi},\,t+\delta_t)-f(\boldsymbol{x},\,\boldsymbol{\xi},\,t) = -\frac{1}{\tau}[f(\boldsymbol{x},\,\boldsymbol{\xi},\,t)-f^{(0)}(\boldsymbol{x},\,\boldsymbol{\xi},\,t)]+J'(\boldsymbol{x},\,\boldsymbol{\xi},\,t)\,\delta_t-\boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f(\boldsymbol{x},\,\boldsymbol{\xi},\,t)\,\delta_t\,, \tag{3.2}$$

where $\tau \equiv \lambda/\delta_t$ is the dimensionless relaxation time. It is obvious that the accuracy of the above equation is only first order in time. Consequently the accuracy of the lattice Boltzmann equations derived from the above equation is also first order in time in principle.

3.2. Low Mach number expansion and phase space discretization. There are two steps in the derivation of lattice Boltzmann equation from Eq. (3.2): (a) construction of an appropriate equilibrium distribution function, and (b) a coherent discretization of phase space. For the isothermal case, the equilibrium distribution function can be obtained by truncation of the Taylor expansion of $f^{(0)}$ up to the second order in $\boldsymbol{u}$:

$$\begin{aligned} f^{(\mathrm{eq})} &= \frac{1}{z}\rho_0(2\pi\theta)^{-D/2}\exp(-U/\theta)\,\exp(-\boldsymbol{\xi}^2/2\theta)\left[1+\frac{(\boldsymbol{\xi}\cdot\boldsymbol{u})}{\theta}+\frac{(\boldsymbol{\xi}\cdot\boldsymbol{u})^2}{2\theta^2}-\frac{\boldsymbol{u}^2}{2\theta}\right] \\ &= \rho\,\omega(\boldsymbol{\xi})\left[1+\frac{(\boldsymbol{\xi}\cdot\boldsymbol{u})}{\theta}+\frac{(\boldsymbol{\xi}\cdot\boldsymbol{u})^2}{2\theta^2}-\frac{\boldsymbol{u}^2}{2\theta}\right], \end{aligned} \tag{3.3}$$

where

$$\omega(\boldsymbol{\xi}) = (2\pi\theta)^{-D/2}\exp\left(-\boldsymbol{\xi}^2/2\theta\right). \tag{3.4}$$

The phase space discretization has to be done in such way that not only all the hydrodynamic moments, but also their corresponding fluxes are preserved *exactly*. This implies that the following quadrature must be evaluated exactly:

$$\int d\boldsymbol{\xi}\,\boldsymbol{\xi}^k\, f^{(\mathrm{eq})}\,, \qquad 0 \le k \le 3\,, \tag{3.5}$$

for isothermal models. (Here we require that not only all the hydrodynamic moments, but also the corresponding fluxes, are computed *exactly* by the quadrature. This requirement is perhaps more stringent than

necessary because energy flux is usually not considered in the isothermal case.) Because of the second order polynomial contained in $f^{(\mathrm{eq})}$ given by Eq. (3.3), the quadrature which must be evaluated exactly is:

$$\int d\boldsymbol{\xi}\, \boldsymbol{\xi}^k \exp(-\boldsymbol{\xi}^2/2\theta)\,, \qquad 0 \le k \le 5\,. \tag{3.6}$$

Because of the exponential function in the above integral, Gaussian quadrature [7] is a natural choice for the evaluation of the integral. With a k-th order polynomial $\psi_k(x)$ of x, Gaussian quadrature defined by the following equation,

$$\int_{-\infty}^{\infty} dx\, \psi_k(x)\, e^{-x^2/2} = \sum_{\alpha=1}^{n} W_\alpha \psi_k(x_\alpha)\,, \tag{3.7}$$

is *exact* for $0 \le k \le 2n-1$, where W_α and x_α are the weights and the abscissas of the quadrature, respectively.

3.3. The forcing term. The forcing term, $\boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f$, must be constructed explicitly in the lattice Boltzmann equation. We use the moment constraint to construct this term. The moments (up to the second order) of the forcing term are:

$$\int d\boldsymbol{\xi}\, \boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f = \int d\boldsymbol{\xi}\, \boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f^{(0)} = 0\,, \tag{3.8a}$$

$$\int d\boldsymbol{\xi}\, \boldsymbol{\xi}\, \boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f = \int d\boldsymbol{\xi}\, \boldsymbol{\xi}\, \boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f^{(0)} = -\rho\boldsymbol{a}\,, \tag{3.8b}$$

$$\int d\boldsymbol{\xi}\, \xi_i\xi_j\, \boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f = \int d\boldsymbol{\xi}\, \xi_i\xi_j\, \boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f^{(0)} = -\rho(a_i u_j + a_j u_i)\,. \tag{3.8c}$$

Here, we have noted that f can be replaced (or approximated) by $f^{(0)}$ without affecting the moments of the forcing term up to the second order in $\boldsymbol{\xi}$ — in general the replacement of f by $f^{(0)}$ does not hold for the moments higher than the third order in $\boldsymbol{\xi}$. This is owing to the fact that f and $f^{(0)}$ have exactly the same conserved (or hydrodynamic) moments, a constraint on the normal solution of the Boltzmann equation in the Chapman-Enskog analysis.

The forcing term, $\boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f$, can be written in terms of an expansion in $\boldsymbol{\xi}$ as follows:

$$\boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f = \rho\,\omega(\boldsymbol{\xi})\left[c^{(0)} + c_i^{(1)}\xi_i + c_{ij}^{(2)}\xi_i\xi_j + \cdots\right]\,, \tag{3.9}$$

where the Einstein notation of summation for the repeated Roman indices i, j, ..., is used. The first few coefficient $c^{(n)}_{i_1 i_2 \cdots i_n}$ can be easily obtained by using the moment constraints given by Eqs. (3.8) if the above expansion is truncated. With the truncated expansion up to the second order in $\boldsymbol{\xi}$ and the first order in $\boldsymbol{u}$, we obtain

$$c^{(0)} = \frac{1}{\xi_T^2}\boldsymbol{a}\cdot\boldsymbol{u}\,, \tag{3.10a}$$

$$c_i^{(1)} = -\frac{1}{\xi_T^2}a_i\,, \tag{3.10b}$$

$$c_{ij}^{(2)} = -\frac{1}{2\xi_T^4}\left(a_i u_j + a_j u_i\right)\,, \tag{3.10c}$$

where $\xi_T \equiv \sqrt{\theta}$ is proportional to the thermal velocity of a particle at temperature T. Therefore, up to the order of $O(u)$ and $O(\xi^2)$, we have

$$\boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f = -\rho\,\omega(\boldsymbol{\xi})\,\xi_T^{-2}\,\left[(\boldsymbol{\xi}-\boldsymbol{u}) + \xi_T^{-2}(\boldsymbol{\xi}\cdot\boldsymbol{u})\,\boldsymbol{\xi}\right]\cdot\boldsymbol{a}\,. \tag{3.11}$$

Note that in the above expansion, only the terms up to the first order in $\boldsymbol{u}$ have been retained, because there is an overall factor of δ_t in the forcing term, as indicated in Eq. (3.2). And δ_t is of $O(u)$ in the Chapman-Enskog analysis for the lattice Boltzmann equation (see Appendix B for explanation). It should be stressed that every term in the Boltzmann equation must be treated equally in terms of maintaining the accuracy. Specifically speaking, the expansion of the forcing term must be of the second order in $\boldsymbol{\xi}$ and the same in the small expansion parameter δ_t, in order to be consistent with the expansion of the equilibrium. It should be noted that there are other methods to compute the expansion of the forcing term. Up to the second order in $\boldsymbol{\xi}$, and the first order in $\boldsymbol{u}$, the expansion of $\boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f^{(0)}$ is identical to that of $\boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f$ because of the constraints given by Eqs. (3.8). Therefore, the result of Eq. (3.11) can be obtained by computing $\boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f^{(0)}$ explicitly.

It should be pointed out that there is another way to include the effect of the forcing due to an external field. Assuming that multi-body interactions among the particles in the system are of short-range and the mean-free-path of a particle is much larger than the interaction range, then a particle is accelerated only by the external field between collisions. Thus the net effect of the acceleration due to the external field during the mean-free-time is an increment of particle velocity. Therefore one can use an equilibrium distribution function with a velocity shift to account for the effect of the forcing due to the external field [66], *i.e.*, $f^{(0)}(\rho, \boldsymbol{u}, \theta)$ becomes $f^{(0)}(\rho, \boldsymbol{u} - \boldsymbol{a}\tau\delta_t, \theta)$ at the presence of the external field. Naturally, the accelerated equilibrium distribution function $f^{(0)}(\rho, \boldsymbol{u}-\boldsymbol{a}\tau\delta_t, \theta)$ leads to a forcing term in the lattice Boltzmann equation when discretized (see Appendix C for details). It should be noted that these two approaches are equivalent up to the first order in δ_t. At higher order of δ_t the velocity shift in the equilibrium distribution will introduce nonlinear terms which are different from what derived from the continuous equation.

3.4. 2D nine-velocity model on square lattice. We now use the 2D nine-velocity LBE model on a square lattice space as a concrete example to illustrate our discretization scheme. A Cartesian coordinate system (in $\boldsymbol{\xi}$-space) is used in this case, and accordingly we set $\psi(\boldsymbol{\xi}) = \xi_x^k \xi_y^l$. Thus the quadrature needed to be evaluated is the following:

$$I = \xi_T^{k+l+2} I_k I_l \,, \tag{3.12}$$

where

$$I_k \equiv \int_{-\infty}^{\infty} d\zeta\, \zeta^k e^{-\zeta^2/2} \,, \tag{3.13}$$

and $\zeta = \xi_x/\xi_T$ or ξ_y/ξ_T. Naturally, the third-order Hermite formula [7] is the optimal choice to evaluate I_k for the purpose of deriving the 9-bit LBE model, *i.e.*, $I_k = \sum_{j=1}^{3} \omega_j \zeta_j^k$. The three abscissas (ζ_j) and the corresponding weights (ω_j) of the quadrature are:

$$\zeta_1 = -\sqrt{3}\,, \quad \zeta_2 = 0\,, \quad \zeta_3 = \sqrt{3}\,, \tag{3.14a}$$

$$\omega_1 = \sqrt{\pi}/6\,, \quad \omega_2 = 2\sqrt{\pi}/3\,, \quad \omega_3 = \sqrt{\pi}/6\,. \tag{3.14b}$$

Then, the integral of Eq. (3.7) becomes:

$$I = 2\xi_T^2 \left[\omega_2^2 \psi(\boldsymbol{0}) + \sum_{\alpha=1}^{4} \omega_1\omega_2 \psi(\boldsymbol{\xi}_\alpha) + \sum_{\alpha=5}^{8} \omega_1^2 \psi(\boldsymbol{\xi}_\alpha) \right] , \tag{3.15}$$

where $\boldsymbol{\xi}_\alpha$ is the zero velocity vector for $\alpha = 0$, one of the vectors of $\sqrt{3}\,\xi_T\,(\pm 1, 0)$ and $\sqrt{3}\,\xi_T\,(0, \pm 1)$ for $\alpha =$ 1–4, and one of the vectors of $\sqrt{3}\,\xi_T\,(\pm 1, \pm 1)$ for $\alpha =$ 5–8. Note that the above quadrature is exact for the integral defined by Eq. (3.13) when $k \leq 5$.

Now momentum space is discretized with nine discrete velocities $\{\boldsymbol{\xi}_\alpha | \alpha = 0, 1, \cdots, 8\}$. To obtain the 9-bit model, configuration space is discretized accordingly, *i.e.*, it is discretized into a square lattice space with a lattice constant $\delta_x = \sqrt{3}\,\xi_T\,\delta_t$. It should be stressed that the temperature T (or θ) is a constant here because we are only dealing with an isothermal model. We can therefore choose δ_x to be a fundamental quantity instead, thus $\sqrt{3}\,\xi_T = c \equiv \delta_x/\delta_t$, or $\theta = \xi_T^2 = c^2/3$. Thus, phase space is discretized coherently: the discretizations of the velocity space and the configuration space are closely coupled together. This is one feature of the lattice Boltzmann equation distinctive from other finite difference schemes.

By comparing Eqs. (3.7) and (3.15), we can identify the weights defined in Eq. (3.7):

$$W_\alpha = 2\pi\,\xi_T^2\,\exp(\boldsymbol{\xi}_\alpha^2/2\xi_T^2)\,w_\alpha\,, \tag{3.16}$$

where

$$w_\alpha = \begin{cases} 4/9, & \alpha = 0, \\ 1/9, & \alpha = 1,\,2,\,3,\,4, \\ 1/36, & \alpha = 5,\,6,\,7,\,8. \end{cases} \tag{3.17}$$

Then, the equilibrium distribution function for the 9-bit model is:

$$f_\alpha^{(\mathrm{eq})} = W_\alpha\,f^{(\mathrm{eq})}(\boldsymbol{x},\,\boldsymbol{\xi}_\alpha,\,t) = w_\alpha\,\rho\,\left[1 + \frac{3(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})}{c^2} + \frac{9(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})^2}{2c^4} - \frac{3\boldsymbol{u}^2}{2c^2}\right], \tag{3.18}$$

where

$$\boldsymbol{e}_\alpha = \begin{cases} (0,\,0), & \alpha = 0\,, \\ (\cos\phi_\alpha,\,\sin\phi_\alpha)\,c, & \alpha = 1\,2,\,3,\,4, \\ (\cos\phi_\alpha,\,\sin\phi_\alpha)\,\sqrt{2}\,c, & \alpha = 5,\,6,\,7,\,8, \end{cases} \tag{3.19}$$

and $\phi_\alpha = (\alpha - 1)\pi/2$ for $\alpha = 1$–4, and $\phi_\alpha = (\alpha - 5)\pi/2 + \pi/4$ for $\alpha = 5$–8.

3.5. Discretized forcing term. Applying the same discretization to the forcing term of Eq. (3.11), we have the discretized forcing term for the nine-velocity model:

$$F_\alpha = -3\,w_\alpha\,\rho\,\left[\frac{1}{c^2}(\boldsymbol{e}_\alpha - \boldsymbol{u}) + 3\frac{(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})}{c^4}\,\boldsymbol{e}_\alpha\right]\cdot\boldsymbol{a}\,. \tag{3.20}$$

The forcing in the above equation satisfies the following constraints:

$$\sum_\alpha F_\alpha = 0\,, \tag{3.21a}$$

$$\sum_\alpha \boldsymbol{e}_\alpha\,F_\alpha = -\rho\,\boldsymbol{a}\,, \tag{3.21b}$$

$$\sum_\alpha \boldsymbol{e}_{\alpha,i}\boldsymbol{e}_{\alpha,j}\,F_\alpha = -\rho\,(u_i a_j + u_j a_i)\,. \tag{3.21c}$$

The above constraints are the discrete counterpart of Eqs. (3.8). If only the first two moment equations in Eqs. (3.21) are to be satisfied, and the third constraint of Eq. (3.21c) is replaced by

$$\sum_\alpha \boldsymbol{e}_{\alpha,i}\boldsymbol{e}_{\alpha,j}\,F_\alpha = 0\,, \tag{3.22}$$

the forcing term thus reduces to

$$F_\alpha = -3\,w_\alpha\,\rho\,\frac{(\boldsymbol{e}_\alpha\cdot\boldsymbol{a})}{c^2}\,. \tag{3.23}$$

The above forcing term is what has been often used for constant body force in the literature [41, 42]. One adverse consequence of using the above forcing term is that the Galilean invariance is lost if $\boldsymbol{a}$ is not a constant in space. In addition, the work by forcing, $\rho \boldsymbol{a} \cdot \boldsymbol{u}$, does not appear in the energy balance equation, and thus leads to an incorrect energy balance equation. As shown in Sec. 5, the forcing terms of similar forms are used to produce various non-ideal gas effects in previous models [59, 60, 62, 61, 51, 50, 27].

3.6. The lattice Boltzmann equation. The additional collision term, J' of Eq. (2.2b), can be explicitly written in the discrete form:

$$J'_\alpha = -f^{(0)}\, b\rho\, g\, (\boldsymbol{e}_\alpha - \boldsymbol{u})\cdot\nabla \ln(\rho^2 g)\,. \tag{3.24}$$

With the discretized J' included, the lattice Boltzmann equation for dense gases is:

$$\begin{aligned} f_\alpha(\boldsymbol{x} + \boldsymbol{e}_\alpha\delta_t,\, t+\delta_t) - f_\alpha(\boldsymbol{x},\, t) = -\frac{g}{\tau}\left[f_\alpha(\boldsymbol{x},\, t) - f_\alpha^{(\mathrm{eq})}(\boldsymbol{x},\, t)\right] \\ -b\,\rho\, g\, f_\alpha^{(\mathrm{eq})}(\boldsymbol{x},\, t)\,(\boldsymbol{e}_\alpha - \boldsymbol{u})\cdot\nabla(\rho^2 g) - F_\alpha\,\delta_t\,, \end{aligned} \tag{3.25}$$

where the forcing term, F_α, is given by Eq. (3.20). The hydrodynamic moments in the lattice Boltzmann models are given by

$$\rho = \sum_\alpha f_\alpha = \sum_\alpha f_\alpha^{(\mathrm{eq})}\,, \tag{3.26a}$$

$$\rho\boldsymbol{u} = \sum_\alpha \boldsymbol{e}_\alpha f_\alpha = \sum_\alpha \boldsymbol{e}_\alpha f_\alpha^{(\mathrm{eq})}\,, \tag{3.26b}$$

$$\rho\theta = \frac{1}{2}\sum_\alpha (\boldsymbol{e}_\alpha - \boldsymbol{u})^2 f_\alpha = \frac{1}{2}\sum_\alpha (\boldsymbol{e}_\alpha - \boldsymbol{u})^2 f_\alpha^{(\mathrm{eq})}\,. \tag{3.26c}$$

The additional collision term, J'_α, involves the density gradient, $\nabla\rho$, which can be explicitly computed by either the second order central differencing

$$\boldsymbol{e}_\alpha\cdot\nabla\rho(\boldsymbol{x})\,\delta_t = \frac{1}{2}[\rho(\boldsymbol{x} + \boldsymbol{e}_\alpha\delta_t) - \rho(\boldsymbol{x} - \boldsymbol{e}_\alpha\delta_t)]\,,$$

or the first order differencing

$$\boldsymbol{e}_\alpha\cdot\nabla\rho(\boldsymbol{x})\,\delta_t = \rho(\boldsymbol{x} + \boldsymbol{e}_\alpha\delta_t) - \rho(\boldsymbol{x})\,.$$

The other alternative would be to construct a collision term similar to the original Enskog collision term given by Eq. (2.1b) without the Taylor expansion in space.

4. The Hydrodynamics and Thermodynamics. Through the Chapman-Enskog analysis (see Appendix B for the details), the hydrodynamic equations of the lattice Boltzmann model for dense gases, given by Eq. (3.25) with the equilibrium of Eq. (3.18), are:

$$\partial_t\rho + \nabla\cdot(\rho\boldsymbol{u}) = 0\,, \tag{4.1a}$$

$$\partial_t\boldsymbol{u} + \boldsymbol{u}\cdot\nabla\boldsymbol{u} = -\frac{1}{\rho}\nabla P + \nu\nabla^2\boldsymbol{u} + \boldsymbol{a}\,, \tag{4.1b}$$

where the viscosity

$$\nu = \frac{(2\tau - g)}{6g}c\delta_x\,. \tag{4.2}$$

and the pressure (or the equation of state) is given by

$$P = \rho\,\theta\,(1 + b\rho\,g)\,. \tag{4.3}$$

With the above equation of state, the sound speed, c_s, becomes

$$c_s^2 = \theta\,\left[1 + b\,\frac{d}{d\rho}(\rho^2 g)\right]\,. \tag{4.4}$$

For ideal gas, $b = 0$ and $g = 1$, P, ν, and c_s recover the previous results for ideal gas. The dependence of the viscosity, ν, on g can be removed by replacing g in the BGK collision term by 1.

Although in the original work of Enskog [5], g only accommodates the volume exclusion effect, or repulsive interaction, in the gas of hard spheres, however there is no reason to prohibit the inclusion of a more general interaction. Indeed, g can be somewhat arbitrary, depending on the interaction. The radial distribution function g provides a freedom to alter the transport coefficients (ν and c_s) as well as the equation of state. However, it should be stressed that there are bounds to this freedom. From Eq. (4.2), it becomes obvious that the model is stable if and only if $\tau > g/2$. This suggests that g also affects the numerical stability of the system. In addition, the sound speed can be changed by g. But one must not expect to achieve $c_s \geq c = \delta_x/\delta_t$ or the basic principle of physics would be violated, because c limits the speed of information propagation in the LBE system. Therefore, there are bounds to the values of g and derivative of $\rho^2 g$.

With the equation of the state given, the Helmholtz free energy density can be given by:

$$\psi(\rho) = \rho \int \frac{P}{\rho^2} d\rho = \rho\,\theta\,\left[\ln\rho + b\int g d\rho\right]\,, \tag{4.5}$$

because

$$P = \rho\frac{d\psi}{d\rho} - \psi\,. \tag{4.6}$$

And the radial distribution function g can also be computed from either P or ψ. That is, with either P or ψ given, one can derive all the relevant thermodynamic quantities from the free energy ψ. For example, given the van der Waals equation of state:

$$P = \rho\,\theta\,\left[\frac{1}{(1-b\rho)} - \frac{a}{\theta}\rho\right]\,, \tag{4.7}$$

where parameter a accounts for the mean result of attractive potential among particles [5], and according to Eqs. (4.3) and (4.7) the radial distribution function g is

$$g = \frac{1}{(1-b\rho)} - \frac{a}{b\,\theta}\,.$$

And the corresponding free energy density is

$$\psi = \rho\,\theta\,\left[\ln\left(\frac{\rho}{1-b\rho}\right) - \frac{a}{\theta}\rho\right]\,.$$

With the free energy and the equation of state defined, the Maxwell construction [32] to determine the co-existence curve becomes physically meaningful and consistent. Nevertheless, care must be taken in conducting the Maxwell construction in the discretized situation. The phenomena of liquid-gas phase transition can be simulated by the model by charging the value of $b\int g d\rho$ (or simply just b) in the free energy density ψ relative to the temperature θ, as indicated by Eq. (4.5). Bear in mind that the temperature θ cannot be changed, because it is a fixed constant in the isothermal LBE models. It should be noted that g should be computed with a given potential in principle. The above manipulation to obtain g is not based upon principles of physics. Also, the use of the free energy adds nothing to the physics of the model, it only reflects a matter of custom or preference.

5. Analysis of Some Existing Models. What we propose in this work is a systematic construction of the lattice Boltzmann equation in a consistent and *a priori* fashion, with the premise that the continuous Boltzmann equation is adequate to describe underlying physics of the systems of interest. In particular, for non-deal gases, one must use the Enskog equation for dense gases instead of the original Boltzmann equation for dilute gases. In light of this view point, a survey of the existing LBE models for non-ideal gases is now in order. We discuss two lattice Boltzmann models for non-ideal gases which are independently proposed by Shan and Chen [59, 60], and by Swift, Osborn, and Yeomans [62, 61]. In spite of the significant differences in their appearances and in technical details, these models do share one common feature in their constructions of the lattice Boltzmann model for non-ideal gases: The derivation of the lattice Boltzmann models is mainly accomplished by constructing a phenomenological equilibrium distribution function which can accommodate non-ideal gas effects and satisfies all the conservation constraints, and therefore leads to hydrodynamics. In what follows, we shall analyze these two models and explicitly demonstrate the difference between the model derived in this paper and the aforementioned two.

5.1. Model with interacting potential. In the model proposed by Shan and Chen [59, 60], a local density-dependent potential $U(\rho(\boldsymbol{x})) \sim \mathcal{G}\theta\psi^2(\rho)$ is explicitly given, where $\mathcal{G}$ is the interaction strength and ψ is an arbitrary function of density ρ. The change of the particle velocity $\boldsymbol{\xi}$ (not the macroscopic velocity $\boldsymbol{u}$) due to $U(\boldsymbol{x})$ is

$$\delta\boldsymbol{\xi} = -\nabla U(\boldsymbol{x})\,\tau\delta_t = \boldsymbol{a}\,\tau\delta_t\,,$$

and $\delta\boldsymbol{u} = -\delta\boldsymbol{\xi}$ is explicitly substituted into the equilibrium distribution function, *i.e.*,

$$\begin{aligned} f_\alpha^{(\mathrm{eq})} &= w_\alpha\,\rho\left\{1+\frac{3[\boldsymbol{e}_\alpha\cdot(\boldsymbol{u}-\boldsymbol{a}\tau\delta_t)]}{c^2}+\frac{9[\boldsymbol{e}_\alpha\cdot(\boldsymbol{u}-\boldsymbol{a}\tau\delta_t)]^2}{2c^4}-\frac{3(\boldsymbol{u}-\boldsymbol{a}\delta_t)^2}{2c^2}\right\} \\ &= w_\alpha\,\rho\left[1+\frac{3(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})}{c^2}+\frac{9(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})^2}{2c^4}-\frac{3\boldsymbol{u}^2}{2c^2}\right]-3\,w_\alpha\,\rho\left[\frac{1}{c^2}(\boldsymbol{e}_\alpha-\boldsymbol{u})+3\frac{(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})}{c^4}\boldsymbol{e}_\alpha\right]\cdot\boldsymbol{a}\,\tau\delta_t \\ &\quad -\frac{3}{2}\,w_\alpha\,\rho\left[\frac{\boldsymbol{a}^2}{c^2}-\frac{(\boldsymbol{e}_\alpha\cdot\boldsymbol{a})^2}{c^4}\right]\tau^2\delta_t^2\,. \end{aligned} \tag{5.1}$$

In the above result, the first part is the usual equilibrium distribution function which has an ideal gas equation of state built in, and the second part accounts for the interaction or non-ideal gas effects, which is identical to the forcing term given by Eq. (3.20), produced by the forcing term $\boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}}f$ in the streaming operator. By combining the forcing with the pressure term in the Navier-Stokes equation, the equation of the state becomes $P = \rho\,[\theta + U(\rho)]$. Thus, non-ideal gas effects are obtained through the phenomenological potential U. To achieve the purpose of mimicking non-ideal gas effects, the leading term in the density expansion of U has to be of second-order in ρ, *i.e.*, $U \sim \mathcal{G}\theta\rho^2$, or $\psi \sim \rho$, as specifically indicated in [59, 60]. Obviously, the potential $U(\rho(\boldsymbol{x}))$ is intended to be the inter-particle interaction. However, it is mathematically implemented as an external field such that its only effect is producing a term ∇U in the momentum equation [59, 60]. The consequence of this conceptual confusion is that the energy balance equation is incorrect, because the result of an external field is the work of $\rho\,\boldsymbol{a}\cdot\boldsymbol{u}$, while the result of the inter-particle interaction is a heat-transfer due to the viscous effect, as shown in Appendix B. Specifically, in the energy equation, the correct term related to the pressure is $P\nabla\cdot\boldsymbol{u}$, where pressure is exactly the one that appears in the momentum equation. However, with the one-body interaction, this becomes $\rho\,\theta\,\nabla\cdot\boldsymbol{u} + \rho\nabla U\cdot\boldsymbol{u}$, *i.e.*, the equation of state is not the same in the momentum equation and the energy equation. Furthermore, the third part in Eq. (5.1), which is proportional to δ_t^2 and nonlinear in $\boldsymbol{a}$, is omitted. This term can be significant when δ_t is set to

unity, as it is a common practice in the lattice Boltzmann simulations. It should also be pointed out that the viscosity in this model remains intact — it is not affected by the potential U.

We have also noted a recent attempt to theoretically justify the model of Shan and Chen [27]. With some crude approximations [27], He *et al.* showed that a desirable forcing term to mimic non-ideal gas effects is $F_\alpha \sim f_\alpha^{(\mathrm{eq})}\,(\boldsymbol{e}_\alpha - \boldsymbol{u})\cdot\boldsymbol{F}\delta_t$, where $\boldsymbol{F} \sim -\nabla V - b\rho\theta g \nabla \ln(\rho^2 g)$, and $V = -2a\rho - \kappa\nabla^2\rho$ accounts for the attractive part in the inter-particle interaction. Without any surprise, this model reproduces an anticipated non-ideal gas equation of state, $P \approx \rho\,\theta\,(1 + b\rho g) + \rho V$, and avoids the nonlinear term of δ_t^2 in the model of interacting potential, as expected. However, the energy balance equation from this model is still incorrect, due to the similarity to the previous model. It should also be noted that it is conceptually incorrect to write the pressure as $P \approx \rho\,\theta\,(1 + b\rho g) + \rho V$. One correct way to generalize the van der Waals equation of state is writing it as the following [4]:

$$P + a\rho^2 = \theta\rho\,(1 + b\rho g)\,, \tag{5.2}$$

where parameter a is related to the two-body interaction potential by:

$$a = -\frac{2}{3}\frac{\pi}{m^2}\int \frac{dV(r)}{dr}\,r^3 dr\,. \tag{5.3}$$

In the Enskog equation, g is obtained from a hard-sphere gas, thus the attractive potential has to be inserted through parameter a.

It is clear that the inter-particle interactions are conceived mathematically as external fields in the aforementioned models. Perhaps the only plausible justification for this view is that the inter-particle interaction can be approximated by a self-consistent one-body interaction field (as in the Vlasov approximation for Coulomb gases). In this case,

$$\int d\boldsymbol{x}_2 d\boldsymbol{\xi}_2\,\nabla_2 V_{12}\cdot\nabla_{\boldsymbol{\xi}} f_2(\boldsymbol{x},\,\boldsymbol{\xi},\,\boldsymbol{x}_2,\,\boldsymbol{\xi}_2,\,t)\nabla_{\boldsymbol{\xi}} f(\boldsymbol{x},\,\boldsymbol{\xi},\,t)\cdot\int d\boldsymbol{x}_2 d\boldsymbol{\xi}_2\,f(\boldsymbol{x}_2,\,\boldsymbol{\xi}_2,\,t)\nabla_2 V_{12} = \nabla_{\boldsymbol{\xi}} f\cdot\nabla\bar{U}\,, \tag{5.4}$$

where the Boltzmann approximation has been invoked, and

$$\nabla\bar{U} = \int d\boldsymbol{x}_2 d\boldsymbol{\xi}_2\,f(\boldsymbol{x}_2,\,\boldsymbol{\xi}_2,\,t)\nabla_2 V_{12}$$

defines the self-inconsistent mean-field potential $\bar{U}$. This approximation is justified for rarefied collisionless plasma with Coulomb interactions, and is simply inappropriate for non-ideal gas systems.

5.2. Model with free energy. A comparison with the model proposed in [62, 61] is slightly more elaborate. Stressing the consistency of thermodynamics in the lattice Boltzmann equation and being inspired by Cahn-Hilliard's model for surface tension [3, 13], the model proposed by Swift *et al.* [62, 61] starts with a free energy functional:

$$\Psi = \int d\boldsymbol{x}\left[\frac{\kappa}{2}\|\nabla\rho\|^2 + \psi(\rho)\right]\,, \tag{5.5}$$

where ψ is the bulk free energy density. The free energy functional in turn determines the diagonal term of the pressure tensor:

$$P = \rho\frac{\delta\Psi}{\delta\rho} - \Psi = p - \kappa\rho\nabla^2\rho - \frac{\kappa}{2}\|\nabla\rho\|^2\,, \tag{5.6}$$

where

$$p = \rho\frac{d\psi}{d\rho} - \psi \tag{5.7}$$

is the equation of state of the fluid. The full pressure tensor is given by

$$\mathsf{P}_{ij} = P\,\delta_{ij} + \kappa\,\partial_i\rho\,\partial_j\rho\,. \tag{5.8}$$

With the pressure tensor given, the equilibrium distribution function is constructed such that not only it satisfies the conservation constraints of Eqs. (3.26), but it also produces the above pressure tensor by enforcing additional constrains $\sum_\alpha f_\alpha^{(\mathrm{eq})} \boldsymbol{e}_{\alpha,i}\boldsymbol{e}_{\alpha,j} = \mathsf{P}_{ij}$ [62, 61], even though Eq. (5.8) is fundamentally incorrect.

To make our analysis as transparent as possible, it is crucial to make an explicit connection between the model of Swift *et al.* to the model of Shan and Chen. The equilibrium distribution function in the model of Swift *et al.* with triangular lattice [62, 61] can be rewritten as follows:

$$\begin{aligned} f_\alpha^{(\mathrm{eq})} &= \frac{1}{3}\,\rho\left[1 + (\boldsymbol{e}_\alpha\cdot\boldsymbol{u}) + 2(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})^2 - \frac{1}{2}\boldsymbol{u}^2\right] \\ &+\frac{\kappa}{3}\left\{(\boldsymbol{e}_{\alpha,x}^2 - \boldsymbol{e}_{\alpha,y}^2)\,\left[(\partial_x\rho)^2 - (\partial_y\rho)^2\right] + 2\boldsymbol{e}_{\alpha,x}\boldsymbol{e}_{\alpha,y}\partial_x\rho\,\partial_y\rho\right\} - \frac{\kappa}{3}\,\rho\,\nabla^2\rho + \frac{1}{3}[\rho\psi'(\rho) - \psi(\rho) - \rho] \end{aligned} \tag{5.9}$$

where $c = \delta_x/\delta_t$ is assumed to be unity. The term in brackets [ ] is nothing but the usual equilibrium distribution function of the 7-bit model [25, 26]. The term in bracket { } is an expression for the tensor $E_{ij} \equiv (\boldsymbol{e}_{\alpha,i}\partial_i\rho)(\boldsymbol{e}_{\alpha,j}\partial_j\rho)$ written in terms of a traceless and an off-diagonal part with correct symmetry such that all the terms proportional to κ reduce to the term $\kappa[\rho\nabla^2\rho + \|\nabla\rho\|^2/2]$ in the diagonal part of the pressure tensor, given by Eq. (5.6). This term is directly taken from Cahn-Hilliard's model and it induces surface tension due to density gradient in addition to the part due to the (non-ideal gas) equation of state, but it does not contribute to the hydrodynamic pressure (or the equation of state). The non-ideal gas part in the equation of state is contained in the last part the above equation: $[\rho\psi'(\rho) - \psi(\rho) - \rho]/3$, which can be written in a density expansion in general:

$$\theta\,\varphi \equiv \frac{1}{3}[\rho\psi'(\rho) - \psi(\rho) - \rho] = \theta\,\rho^2\,(B + C\rho + \cdots) \tag{5.10}$$

where coefficients B, C, $\cdots$ are virial coefficients. We have noted that only the leading term in the density expansion of φ, $B\rho^2$, is needed in order to capture the non-ideal gas effects, for this term not only leads to a non-ideal gas equation of state, but also provides all the necessary terms to control the surface tension in Cahn-Hilliard's model, because $\nabla\nabla\rho^2 = 2(\rho\nabla^2\rho + \|\nabla\rho\|^2)$. By comparing Eq. (5.9) to Eq. (5.1), the connection between the model of Swift *et al.* and the model of Shan and Chen becomes obvious if Eq. (3.23) for the forcing term is used and the equivalence of $\theta\,\varphi = \boldsymbol{e}_\alpha\cdot\nabla U \sim F_\alpha$ is established. Thus, the model of Swift *et al.* uses Eq. (3.23) for the forcing term, which is only valid for a constant body force, whereas the model of Shan and Chen uses Eq. (3.20) for the forcing term. The interaction strength in the model of Swift *et al.* is proportional to temperature θ (which is incorrect for isothermal fluids), whereas in the model of Shan and Chen, it is proportional to a constant $\mathcal{G}$. Since the connection of the two models can be explicitly established, all the analysis in the previous subsection can be immediately applied to the present model.

It should be pointed out that at the level of the Boltzmann equation, the density gradient term, $\|\nabla\rho\|^2$, in the free energy functional has no justification whatsoever within the framework of Chapman-Enskog analysis. [In fact, the density gradient $\nabla\rho$ can only appear in the second order solution of f (the Burnett equation [5]) in the Chapman-Enskog analysis, which is beyond the Navier-Stokes equations.] It is clear that the analysis presented in [62, 61] and the subsequent work [51, 50] does not follow the Chapman-Enskog analysis; therefore, it cannot lead to a mathematically valid derivation of macroscopic equations from the mesoscopic equation. Consequently, the derivation of macroscopic equations from the model becomes dubious, and the model suffers from a number of unexpected adverse effects which are discussed next.

First, the model lacks Galilean invariance, mainly because of the forcing term $F_\alpha \sim \theta\varphi$. This defect can be fixed by using a correct forcing term according to Eq. (3.20): $F_\alpha \sim \rho[(\boldsymbol{e}_\alpha - \boldsymbol{u}) + 3(\boldsymbol{e}_\alpha \cdot \boldsymbol{u})\boldsymbol{e}_\alpha] \cdot \nabla\varphi$. However, there are other terms involving the density gradient which also cause the problem of lack of Galilean invariance [31]. Second, the ratio between the number of rest particles and the number of moving particles depends on the local density gradient. It can be shown that this ratio is related to temperature, because in the two-speed system, the width of the equilibrium distribution, which is the temperature, is determined by this ratio. [To be exact, according to the definition of ω, Eq. (3.4), the ratio $\omega(0)/\omega(\boldsymbol{c}) = e^{c^2/2\theta}$, which must be a constant in isothermal fluids.] This means that the temperature may vary locally depending on the density gradient while the model is claimed to simulate an isothermal fluid. Again, this problem can be fixed by using the correct forcing term aforementioned. In addition, the model cannot lead to the correct energy balance equation for the very same reason, as shown in the previous subsection, that the terms related to the free energy can be considered as a body-force due to a thermodynamic potential (free energy in the model) which is a mean-field quantity.

We stress that the conceptual difficulty caused by the confusion between body-force and interaction cannot be circumvented by technical tricks such as using a correct forcing term, or including higher order terms in $\boldsymbol{u}$ in the equilibrium distribution function $f_\alpha^{(\mathrm{eq})}$. The reason is obvious: as long as a mean-field potential, whether an interaction or a free energy, is employed to mimic non-ideal gas effects, the constraints of Eqs. (3.8) must be satisfied, therefore the inconsistency of the pressure between the momentum equation and the energy equation arises, regardless of the order (in $\boldsymbol{u}$) of the equilibrium distribution function — this is true even in the continuum case. Furthermore, certain terms in the pressure tensor, P_{ij}, were arbitrarily omitted in the Navier-Stokes equation derived from the model [62, 61]. Therefore, the use of P_{ij} is *ad hoc* at best. Following the above analysis, one can also conclude that the multi-component model constructed in the same manner [51, 50] suffers from the same problems. One distinctive feature of this model is that, by using Cahn-Hilliard's model, the surface tension can be controlled independently of the equation of state by the density gradient. This appears to be the reason why the spurious mass flux is reduced in this model [62, 61].

Most likely, the aforementioned problems were not discovered in [62, 61, 51, 50], because all the tests conducted in [62, 61, 51, 50] were not designed to test hydrodynamics *per se*, they were designed to test other properties such as the equilibrium density profiles and Laplace's law, which are related more to spinodal decomposition than to hydrodynamics, and can be well produced by other lattice Boltzmann models [21, 18, 19, 20, 46], or even models without hydrodynamics, such as Cahn-Hilliard's model [3, 13]. In fact, it has been shown that the model of Swift *et al.* does not satisfy the Navier-Stokes equation, in either the bulk region or interface region, although it does possess conserved quantities [31]. Numerous simple hydrodynamic tests showed that the departure of the model from the Navier-Stokes equation is quite significant both quantitatively and qualitatively [31]. For instance, when the model is used to simulate a simple hydrodynamic problem such as a single droplet subject to shear [64], the simulation [64] does not produce any credible quantitative hydrodynamic results because the model does not even satisfy the Navier-Stokes equation. The best that the kind of simulations presented in a recent work by Wagner and Yeomans [64] can provide is some vague, poor, qualitative description of flow phenomena, which is often incorrect. Therefore we doubt the validity of numerical predictions made by the model.

It should also be noted that the Hamiltonian approach [59, 60] and the free energy approach [62, 61, 51, 50] are indeed equivalent in terms of phenomenology. Given a Hamiltonian $\mathcal{H}$ of an interacting N-particle

system, the corresponding free energy Ψ can be obtained *via* the partition function based upon $\mathcal{H}$:

$$\mathcal{H} = \sum_{i=1}^{N} \left[\frac{1}{2} m_i \boldsymbol{\xi}_i^2 + U(\boldsymbol{x}_i) \right] + \sum_{i<j} V(|\boldsymbol{x}_i - \boldsymbol{x}_j|) \,, \tag{5.11}$$

where $\boldsymbol{\xi}_i$ and $\boldsymbol{x}_i$ are the phase space of the i-the particle, m_i is the particle mass, $U(\boldsymbol{x}_i)$ is an external field and $V(|\boldsymbol{x}_i - \boldsymbol{x}_j|)$ is a mean-field two-body interaction potential, the partition function is

$$Z = \int d\boldsymbol{x} d\boldsymbol{\xi} \exp(-\mathcal{H}/k_B T) \,, \tag{5.12}$$

where $(\boldsymbol{x}, \boldsymbol{\xi})$ represents the entire phase space of the N-particle system. Consequently, the free energy is given by

$$\Psi = -k_B T \ln Z \,. \tag{5.13}$$

Thus, in principle information is neither gained nor lost whether the problem is formulated in terms of $\mathcal{H}$ or Ψ. One cannot claim that using the free energy and utilizing the Maxwell construction leads to a better or more physical model. Perhaps the only advantage of using the free energy is that Ψ is a global state variable and therefore it is independent of coordinates. However, this advantage bears no relevance in the LBE models. In light of the thorough analysis provided above, we conclude that the claim made by Swift [62, 61] *et al.* that "*we show for the first time that it is possible to set up a lattice Boltzmann scheme modeling isothermal hydrodynamics for two-phase systems*" is unfounded.

In summary, the main difference between the model derived from the Enskog equation and the existing ones is in the physics. Our starting point is the Enskog equation for dense gases in which the non-ideal gas effects are naturally considered, whereas in all other existing models [59, 60, 62, 61, 51, 50, 27], the starting point is the original Boltzmann equation which is only suitable for dilute gases (ideal gases). Beginning with incorrect physics, one has no choice but to invoke various *ad hoc* approximations. Inevitably, various defects exist in the aforementioned models. One notable feature common to these models is that the viscosity is independent of non-ideal gas effects, which is inconsistent with the Enskog equation.

6. Conclusion. We are now in the position to lay out the procedure for constructing a thermodynamically consistent lattice Boltzmann equation for non-ideal gases. Given inter-particle interactions, the radius distribution function g can be computed in principle, and the collision term in the Enskog equation, J', can be constructed. This collisional term would correctly produce the non-ideal gas effects. With this term implemented in the lattice Boltzmann model, a thermodynamic and hydrodynamic consistency can be achieved in the sense of the finite difference approximation. With g given, the free energy density, ψ, can be obtained explicitly. Subsequently, other pertinent thermodynamic quantities such as the equation of state, pressure tensor, surface tension, and so on, can be directly and easily derived from the free energy while the correct hydrodynamics is preserved in the lattice Boltzmann equation.

It should be emphasized that because the Boltzmann equation describes mesoscopic dynamics, the constraints imposed on it must be compatible with the mesoscopic dynamics. Specifically speaking, given an arbitrary interaction in a system, one can *in principle* compute the equation of state (*e.g.*, by means of the virial expansion). This is an averaging process, because macroscopic observables (the equation of state, surface tension, *etc.*) are averaged macroscopic quantities. But, the reverse are not true in general: given an arbitrary equation of state, one may not be to able to uniquely find a corresponding interaction in the mesoscopic description. However, this can be achieved in the formalism of the lattice Boltzmann equation,

owing to the simple structure of the formalism. Nevertheless, the simplicity of the LBE method does not comes without a price — the inconsistency in the LBE thermodynamics and discrete effects are inherent to the LBE models. In contrast to the LBE method, it is also worth while to mention some new approaches more closely related to standard computational fluid dynamics methods [34, 49, 33] which show promise for dealing with the interfacial problems.

It is a fair observation that so far a large part of the lattice Boltzmann enterprise rests upon the phenomenology of creating various "new" equilibrium distribution functions to accommodate different physical phenomena ranging from non-ideal gases or multi-component fluids to visco-elastic media [55]. Previous procedures to construct the equilibrium distribution can be summarized as follows. By observing the hydrodynamic equations of a system of interest, one can anticipate those terms in the equilibrium distribution which are necessary to produce the desired results (usually a desirable stress tensor). Then proportionality factors for these terms are determined by the conservation constraints. It is evident that this approach lacks mathematical rigor and that the models derived in this fashion may suffer from artificial defects which are uncontrollable, such as the models in Refs. [62, 61, 51, 50, 55]. The problem common to these models is that the mathematical rigor of the Chapman-Enskog analysis has been completely ignored, as typified by the work in [62, 61].

It is important to point out that the rigor of the Chapman-Enskog analysis can be retained without following the viewpoint of deriving lattice Boltzmann models *via* discretization of the corresponding continuous kinetic equation. Given a set of discrete velocities on a lattice space with a collision operator obeying conservation laws and associated symmetries, an orthogonal basis spanned by the eigenvectors of the collision operator can be obtained [8, 16, 17]. The kinetic modes of the basis, which are fluxes, can have different relaxation times [8, 16, 17]. Not only does this approach overcome some shortcomings of the single relaxation time method such as a fixed Prandtl number, but it also follows the Chapman-Enskog analysis rigorously. We suspect that this approach may be equivalent to a discrete version of the hierarchy of kinetic equations proposed by Levermore [39].

In this paper we carry out a systematic derivation of the lattice Boltzmann equation for non-ideal gases from the Enskog equation. It should be stressed that the procedure illustrated here is general and can be easily extended to other lattice Boltzmann models, *e.g.*, multi-component models [21, 18, 19, 20]. This procedure can also be used to improve the accuracy of the lattice Boltzmann models systematically. Our procedure can be briefly summarized as follows. First of all, one can observe the equation of state of a system, and extract the non-ideal gas part in it. This part is related to the radial distribution function g. From g, the additional collision term responsible for it can be constructed. Then one can systematically discretize the Enskog equation with the additional collision term to obtain the corresponding lattice Boltzmann equation. This approach is not only rigorous, but also systematic. The equilibrium distribution is uniquely determined in this procedure. It enables one to see clearly what approximation is made in the derivation of the lattice Boltzmann equation. In this way it can be shown that the accuracy of the lattice Boltzmann equation is indeed first order in time and second order in space [67].

In additional to an *a priori* derivation of the lattice Boltzmann model for non-ideal gases, we explicitly illustrate the differences between our model and existing ones. Based upon our analysis, we can conclude that the problem in the model of interacting potential [59, 60] is a minor one and can be easily fixed by either directly using a forcing term as we proposed, or adding a correction to remove the δ_t^2 dependent terms. In contrast to the model of interacting potential, the model of free energy [62, 61] presents many major problems. It starts with an intention to correct the thermodynamic inconsistency in other models,

but it ends up with more serious inconsistencies, because the pressure tensor in the model is constructed without any physical basis at the level of the Boltzmann equation. It is also important to point out that none of these models can lead to the correct energy balance equation, and therefore they are inconsistent with their continuous counterpart — the Boltzmann equation. Starting with the Enskog equation in the presence of an external field and through a rigorous discretization procedure, we can obtain a consistent thermodynamics and hydrodynamics for non-ideal gases in the sense of the discretizing approximation. With this systematic means, one can use either an interaction or a free energy to obtain the equation of state, that, when incorporated into a collisional term, accounts for non-ideal gas effects among the particles.

Our future work will extend our theory to multi-component fluids, and obtain a consistent thermodynamics for lattice Boltzmann models.

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Appendix A. Modified Boltzmann Equation for Dense Gases.

The Boltzmann equation,

$$\partial_t f + \boldsymbol{\xi}\cdot\nabla f + \boldsymbol{a}\cdot\nabla_{\boldsymbol{\xi}} f = J\,, \tag{A.1}$$

can be modified for dense gas by explicitly considering the volume exclusion effect in the collision term J for hard spheres of radius r_0 as the following [5, 30, 23]:

$$\begin{aligned} J &= \int d\boldsymbol{\mu}_1\ [g(\boldsymbol{x}+r_0\hat{\boldsymbol{r}})f(\boldsymbol{x},\boldsymbol{\xi}')f(\boldsymbol{x}+2r_0\hat{\boldsymbol{r}},\boldsymbol{\xi}_1') - g(\boldsymbol{x}-r_0\hat{\boldsymbol{r}})f(\boldsymbol{x},\boldsymbol{\xi})f(\boldsymbol{x}-2r_0\hat{\boldsymbol{r}},\boldsymbol{\xi}_1)] \qquad \text{(A.2a)}\\ &= J^{(0)} + J^{(1)} + J^{(2)} + \cdots\,, \end{aligned}$$

$$J^{(0)} = g\int d\boldsymbol{\mu}_1 (f'f_1' - ff_1)\,, \tag{A.2b}$$

$$J^{(1)} = r_0\int d\boldsymbol{\mu}_1 (f'f_1' + ff_1)\,\hat{\boldsymbol{r}}\cdot\nabla g\,, \tag{A.2c}$$

$$J^{(2)} = 2r_0 g\int d\boldsymbol{\mu}_1 \hat{\boldsymbol{r}}\cdot(f'\nabla f_1' + f\nabla f_1)\,, \tag{A.2d}$$

where g is the radial distribution function, $\hat{\boldsymbol{r}}$ is the unit vector pointing from the particle f_1 to the particle f, $J^{(n)}$, $n = 0, 1, 2, \ldots$, are obtained by the Taylor expansion of g, $f_1 \equiv f(\boldsymbol{\xi}_1)$, and $f_1' \equiv f(\boldsymbol{\xi}_1')$ in Eq. (A.2a) of J about $\boldsymbol{x}$,

$$d\boldsymbol{\mu}_1 = \|\boldsymbol{\xi}_1 - \boldsymbol{\xi}\|\sigma\, d\Omega d\boldsymbol{\xi}_1\,, \tag{A.3}$$

and σ and Ω are differential collision cross section and the solid angle in coordinate $\boldsymbol{x}$-space. The Enskog equation is also called the modified Boltzmann equation for dense gases in the literature [23].

The term $J^{(0)}$ given by Eq. (A.2b) is the usual collisional term in the Boltzmann equation with an extra factor g, which can be approximated by the BGK approximation, *i.e.*,

$$J^{(0)} = -\frac{g}{\lambda}[f - f^{(0)}], \tag{A.4}$$

where $f^{(0)}$ is the equilibrium distribution function of Maxwell and Boltzmann.

The term $J^{(1)}$ and $J^{(2)}$ can be explicitly evaluated for hard sphere potential. For hard spheres of radius r_0, we have

$$\sigma\, d\Omega = \begin{cases} ds = 2r_0 \cos\vartheta d\vartheta\,, & \text{in 2D,} \\ s\, ds = 2r_0^2 \sin(2\vartheta) d\vartheta d\varphi\,, & \text{in 3D,} \end{cases} \tag{A.5}$$

where ϑ is the azimuthal angle between the z-axis parallel to $(\boldsymbol{\xi}_1 - \boldsymbol{\xi})$ and $(\boldsymbol{\xi}' - \boldsymbol{\xi})$, and $0 \le \vartheta \le \pi/2$, φ is the polar angle on the plane perpendicular to the z-axis, and

$$s = 2r_0 \sin\vartheta \tag{A.6}$$

is the impact parameter in the collision. With the approximation of $f \approx f^{(0)}$ in Eqs. (A.2c) and (A.2d), we have

$$J^{(1)} = -f^{(0)}\, b\, \rho\, (\boldsymbol{\xi} - \boldsymbol{u})\cdot\nabla g\,, \tag{A.7a}$$

$$\begin{aligned} J^{(2)} = -f^{(0)}\, b\, \rho\, g \Bigg[& 2(\boldsymbol{\xi} - \boldsymbol{u})\cdot\nabla \ln\rho + \frac{2}{(D+2)} \frac{(\xi_i - u_i)(\xi_j - u_j)\partial_i u_j}{\theta} \\ & + \left\{ \frac{1}{(D+2)} \frac{(\boldsymbol{\xi} - \boldsymbol{u})^2}{\theta} - 1 \right\} \nabla\cdot\boldsymbol{u} + \frac{1}{2} \left\{ \frac{D}{(D+2)} \frac{(\boldsymbol{\xi} - \boldsymbol{u})^2}{\theta} - 1 \right\} (\boldsymbol{\xi} - \boldsymbol{u})\cdot\nabla \ln\theta \Bigg]\,, \end{aligned} \tag{A.7b}$$

where b is the second virial coefficient, ρ, $\boldsymbol{u}$, and $\theta = k_B T/m$, are mass density, velocity, and normalized temperature of fluid, respectively; m is the particle mass, and D is the dimension of the $\boldsymbol{\xi}$-space. In above equation, the Einstein notation for summation among repeated indices is used. The second virial coefficient for the hard sphere gas is:

$$b = V_0/m\,, \tag{A.8}$$

where V_0 is the volume of a hard sphere, which is $16\pi r_0^3/3$ in 3D, or πr_0^2 in 2D. Note that $b\rho = V_0 n$, where n is the particle number density, is a dimensionless quantity called packing fraction (for the hard-sphere system), and g is a function of $b\rho$.

It should be noted that the collision term, J, in the Enskog equation does not conserve mass, momentum, and energy *locally*, because it involves non-local interactions [5]. However, mass, momentum, and energy are conserved globally. The non-local interaction is expected to produce non-ideal gas effects due to the exclusive volume in momentum and energy equations in hydrodynamics. The first term in the expansion of J, $J^{(0)}$, is the usual collision term in the original Boltzmann equation for dilute gases (multiplied by a factor g), and it conserves mass, momentum, and energy locally. Other terms, $J^{(n)}$ for $n \ge 1$, do not conserve mass, momentum, and energy locally, they are responsible for the flux (of mass, momentum, and energy) transfer due to non-local interactions.

To the first order approximation in the Chapman-Enskog analysis, only $J^{(0)}$, $J^{(1)}$, and $J^{(2)}$ shall be retained in the modified Boltzmann equation for the dense gases. Higher order collisional terms, $J^{(n)}$, $n \ge 3$, are neglected because they are involved higher order or higher power of gradients of ρ, $\boldsymbol{u}$, and θ. The term $J^{(2)}$ can be simplify for incompressible and isothermal fluids. In that case, the last two terms in Eq. (A.7b) vanish. Then the term of $\partial_i u_j$ must be neglected owing to the conservation constraints. The term of $\nabla\rho$ can be included into J' by

$$J' = -f^{(0)}\, b\rho\, (\boldsymbol{\xi} - \boldsymbol{u})\cdot[\nabla g + g\nabla \ln\rho^2] - f^{(0)}\, b\rho\, g\, (\boldsymbol{\xi} - \boldsymbol{u})\cdot\nabla \ln(\rho^2 g)\,. \tag{A.9}$$

It is clear that J' conserves mass locally. However, it is responsible for flux transfer due to the non-local interaction. The first order moment of J', which is the mass flux, gives the part of the equation of state

attributed to non-ideal gas effects:

$$\int d\boldsymbol{\xi}\,\boldsymbol{\xi} J' = -b\rho\, g \int d\boldsymbol{\xi}\, f^{(0)} \boldsymbol{\xi}\,(\boldsymbol{\xi}-\boldsymbol{u})\cdot\nabla \ln(\rho^2 g) \; - b\,\theta\rho^2 g \nabla \ln(\rho^2 g) = -\nabla(\theta\, b\rho^2 g)\,. \tag{A.10}$$

Combining with the ideal gas part of the equation of state, $\rho\theta$, we obtain the total equation of state:

$$P = \rho\,\theta\,(1 + b\rho g)\,. \tag{A.11}$$

For hard sphere gases, the radius distribution function g is known as up to $(b\rho)^3$ [5, 30].

The energy transfer due to the effect of J' is:

$$\frac{1}{2}\int d\boldsymbol{\xi}\,\boldsymbol{\xi}^2 J' = -\frac{1}{2} b\rho\, g \int d\boldsymbol{\xi}\, f^{(0)} \boldsymbol{\xi}^2\,(\boldsymbol{\xi}-\boldsymbol{u})\cdot\nabla \ln(\rho^2 g) \; - \boldsymbol{u}\cdot\nabla(\theta\, b\rho^2 g)\,. \tag{A.12}$$

This correctly corresponds to the non-ideal gas thermal equation of state, Eq. (A.11).

Appendix B. Chapman-Enskog Analysis of Lattice Boltzmann Equation.

By introducing the following expansions [41, 24]:

$$f_\alpha(\boldsymbol{x} + \boldsymbol{e}_\alpha\delta_t,\, t+\delta_t) = \sum_{n=0}^{\infty} \frac{\epsilon^n}{n!} \mathcal{D}_t^n f_\alpha(\boldsymbol{x},\, t)\,, \tag{B.1a}$$

$$f_\alpha = \sum_{n=0}^{\infty} \epsilon^n f_\alpha^{(n)}\,, \tag{B.1b}$$

$$\partial_t = \sum_{n=0}^{\infty} \epsilon^n \partial_{t_n}\,, \tag{B.1c}$$

where $\epsilon = \delta_t$ and $\mathcal{D}_t \equiv (\partial_t + \boldsymbol{e}_\alpha\cdot\nabla)$, we can rewrite the lattice Boltzmann equation with a forcing term

$$f_\alpha(\boldsymbol{x} + \boldsymbol{e}_\alpha\delta_t,\, t+\delta_t) - f_\alpha(\boldsymbol{x},\, t) = -\frac{g}{\tau}[f_\alpha(\boldsymbol{x},\, t) - f_\alpha^{(\mathrm{eq})}(\boldsymbol{x},\, t)] + J'_\alpha\delta_t - F_\alpha\delta_t \tag{B.2}$$

in the consecutive order of the parameter ϵ as follows:

$$\epsilon^0: \quad f_\alpha^{(0)} = f_\alpha^{(\mathrm{eq})}\,, \tag{B.3a}$$

$$\epsilon^1: \quad f_\alpha^{(1)} = -\frac{\tau}{g}\mathcal{D}_{t_0} f_\alpha^{(0)}\,, \tag{B.3b}$$

$$\epsilon^2: \quad f_\alpha^{(2)} = -\frac{\tau}{2g}\left[\mathcal{D}_{t_0}^2 + 2\partial_{t_1}\right] f_\alpha^{(0)} - \frac{\tau}{g}\mathcal{D}_{t_0} f_\alpha^{(1)}\,, \tag{B.3c}$$

where $\mathcal{D}_{t_n} \equiv (\partial_{t_n} + \boldsymbol{e}_\alpha\cdot\nabla)$. Note that both F_α and J'_α in Eq. (B.2) do not appear in the above equations. However, they will appear in the governing equations in what follows. The distribution function f_α is the normal solution which is constrained by:

$$\sum_\alpha f_\alpha^{(0)} \begin{bmatrix} 1 \\ \boldsymbol{e}_\alpha \end{bmatrix} = \begin{bmatrix} \rho \\ \rho\boldsymbol{u} \end{bmatrix}\,, \tag{B.4a}$$

$$\sum_\alpha f_\alpha^{(n)} \begin{bmatrix} 1 \\ \boldsymbol{e}_\alpha \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}\,, \qquad n > 0\,, \tag{B.4b}$$

where the equilibrium $f_\alpha^{(0)}$ (for the 9-bit model) is given by:

$$f_\alpha^{(\mathrm{eq})} = w_\alpha\,\rho\left\{1 + 3\frac{(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})}{c^2} + \frac{9}{2}\frac{(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})^2}{c^4} - \frac{3}{2}\frac{\boldsymbol{u}^2}{c^2}\right\}\,. \tag{B.5}$$

The additional collision term, J'_α, which is responsible for the volume exclusion effect in dense gases, is given by

$$J'_\alpha = -f_\alpha^{(\mathrm{eq})}\, b\, \rho\, g\, (\boldsymbol{e}_\alpha - \boldsymbol{u})\cdot\nabla \ln(\rho^2 g)\,. \tag{B.6}$$

The forcing term, F_α, for the nine-velocity model, is given by,

$$F_\alpha = -3\, w_\alpha\, \rho\, \left[\frac{1}{c^2}(\boldsymbol{e}_\alpha - \boldsymbol{u}) + 3\frac{(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})}{c^4}\,\boldsymbol{e}_\alpha\right]\cdot\boldsymbol{a}\,, \tag{B.7}$$

which satisfies the following constraints:

$$\sum_\alpha F_\alpha = 0\,, \tag{B.8a}$$

$$\sum_\alpha \boldsymbol{e}_\alpha F_\alpha = -\rho\boldsymbol{a}\,, \tag{B.8b}$$

$$\sum_\alpha \boldsymbol{e}_{\alpha,i}\boldsymbol{e}_{\alpha,j} F_\alpha = -\rho\,(u_i a_j + u_j a_i)\,. \tag{B.8c}$$

Also, f_α is a Chapman-Enskog *ansatz*, $f(\boldsymbol{x}, \boldsymbol{\xi}, t) = f(\boldsymbol{x}, \boldsymbol{\xi}; \rho, \boldsymbol{u}, \theta)$, *i.e.*, the temporal dependence of f_α is through the hydrodynamic variables ρ, $\boldsymbol{u}$ and θ. Therefore,

$$\partial_t f_\alpha = \frac{\partial f_\alpha}{\partial \rho}\,\partial_t\rho + \frac{\partial f_\alpha}{\partial \boldsymbol{u}}\,\partial_t\boldsymbol{u} \tag{B.9}$$

for isothermal fluids.

For the 9-bit model, we have:

$$\sum_\alpha f_\alpha^{(0)} = \rho\,, \tag{B.10a}$$

$$\sum_\alpha \boldsymbol{e}_\alpha f_\alpha^{(0)} = \rho\boldsymbol{u}\,, \tag{B.10b}$$

$$\sum_\alpha \boldsymbol{e}_{\alpha,i}\boldsymbol{e}_{\alpha,j} f_\alpha^{(0)} = \theta\rho\delta_{ij} + \rho u_i u_j\,, \tag{B.10c}$$

$$\sum_\alpha \boldsymbol{e}_{\alpha,i}\boldsymbol{e}_{\alpha,j}\boldsymbol{e}_{\alpha,k} f_\alpha^{(0)} = \theta\rho\Delta_{ijkl}\, u_l\,, \tag{B.10d}$$

and

$$\sum_\alpha J'_\alpha = 0\,, \tag{B.11a}$$

$$\sum_\alpha \boldsymbol{e}_\alpha J'_\alpha = -\theta\, b\,\nabla(\rho^2 g)\,, \tag{B.11b}$$

$$\sum_\alpha \boldsymbol{e}_{\alpha,i}\boldsymbol{e}_{\alpha,j} J'_\alpha = b\,[u_i u_j \boldsymbol{u}\cdot\nabla - \theta\,(u_i\partial_j + u_j\partial_i)]\,(\rho^2 g)\,, \tag{B.11c}$$

where δ_{ij} and δ_{ijkl} are the Kronecker delta with two and four indices, respectively, and

$$\Delta_{ijkl} = \delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}\,. \tag{B.12}$$

The governing equations of f_α up to the order of ϵ are:

$$\mathcal{D}_{t_0} f^{(0)} = -\frac{g}{\tau} f^{(1)} + J'_\alpha - F_\alpha\,, \tag{B.13a}$$

$$\partial_{t_1} f^{(0)} + \frac{(2\tau - g)}{2\tau}\mathcal{D}_{t_0} f^{(1)} = -\frac{g}{\tau} f^{(2)}\,. \tag{B.13b}$$

In the derivation of Eq. (B.13b), we have made the following approximation that $\mathcal{D}_{t_0} g \approx 0$, which is accurate up to $O(u^2)$. The moments of the first order governing equation, Eq. (B.13a), lead to the Euler equations:

$$\partial_{t_0} \rho + \nabla\cdot(\rho \boldsymbol{u}) = 0\,, \tag{B.14a}$$

$$\partial_{t_0} (\rho \boldsymbol{u}) + \nabla\cdot\Pi^{(0)} = \boldsymbol{F} - \theta\, b \nabla(\rho^2 g)\,, \tag{B.14b}$$

where $\Pi^{(0)} = \sum_\alpha \boldsymbol{e}_\alpha \boldsymbol{e}_\alpha f_\alpha^{(0)}$ is the zeroth-order momentum flux tensor. With $\Pi_{ij}^{(0)}$ given by Eq. (B.10c), the above equations can be rewritten as:

$$\partial_{t_0} \rho + \nabla\cdot(\rho \boldsymbol{u}) = 0\,, \tag{B.15a}$$

$$\partial_{t_0} \boldsymbol{u} + \boldsymbol{u}\cdot\nabla \boldsymbol{u} = -\frac{1}{\rho}\nabla P + \boldsymbol{a}\,, \tag{B.15b}$$

where $\boldsymbol{a} = \boldsymbol{F}/\rho$ is the acceleration, and

$$P = \rho\,\theta\,(1 + b\rho\, g) \tag{B.16}$$

is the equation of state for non-ideal gas, depending on the radial distribution function g. (Note that for the nine-velocity isothermal model here, $\theta = c^2/3$.)

The moments of the second order governing equation, Eq. (B.13b), lead to the following equations:

$$\partial_{t_1} \rho = 0\,, \tag{B.17a}$$

$$\partial_{t_1} (\rho \boldsymbol{u}) + \frac{(2\tau - g)}{2\tau}\nabla\cdot\Pi^{(1)} = 0\,, \tag{B.17b}$$

where $\Pi^{(1)} = \sum_\alpha \boldsymbol{e}_\alpha \boldsymbol{e}_\alpha f_\alpha^{(1)}$ is the first-order momentum flux tensor. With the aid of Eqs. (B.10) and (B.15), we have:

$$\begin{aligned}\Pi_{ij}^{(1)} &= \sum_\alpha \boldsymbol{e}_{\alpha,i}\boldsymbol{e}_{\alpha,j} f_\alpha^{(1)} = -\frac{\tau}{g}\sum_\alpha \boldsymbol{e}_{\alpha,i}\boldsymbol{e}_{\alpha,j}\mathcal{D}_{t_0} f_\alpha^{(0)} = -\frac{\tau}{g}\left[\partial_{t_0}\Pi_{ij}^{(0)} + \theta\,(\nabla\cdot\rho\boldsymbol{u}\,\delta_{ij} + \partial_i\rho u_j + \partial_j\rho u_i)\right] \\ &= -\frac{\tau}{g}\left[\theta\,(\partial_{t_0}\rho + \nabla\cdot\rho\boldsymbol{u})\,\delta_{ij} + \partial_{t_0}(\rho u_i u_j) + \theta\,(\partial_i\rho u_j + \partial_j\rho u_i)\right] = -\frac{\tau}{g}\theta\,\rho\,(\partial_i u_j + \partial_j u_i) + O(M^3)\,,\end{aligned}$$

where $\partial_i = \partial/\partial x_i$. In the above result of $\Pi_{ij}^{(1)}$, the terms such as $u_i\partial_j\rho$ have been neglected because $\nabla\rho$ is of the order $O(M^2)$, and it is done consistent with the small velocity expansion of $f_\alpha^{(\mathrm{eq})}$ up to the order of $O(\boldsymbol{u}^2)$. [Note that $O(\boldsymbol{u}) = O(M)$, therefore we take the liberty to interchange these notations.] Similarly, we have

$$\begin{aligned}\partial_j\Pi_{ij}^{(1)} &= -\frac{\tau}{g}\theta\,\rho\,\partial_j(\partial_i u_j + \partial_j u_i) + O(M^3) \\ &= -\frac{\tau}{g}\theta\,\rho\,(\partial_i\nabla\cdot\boldsymbol{u} + \nabla^2 u_i) + O(M^3) = -\frac{\tau}{g}\theta\,\rho\,\nabla^2 u_i + O(M^3)\,,\end{aligned} \tag{B.18}$$

where the term $\nabla\cdot\boldsymbol{u}$ has been neglected because it is of $O(M^2)$ due to Eq. (B.15a).

Combining the first and the second order results [Eqs. (B.14) and (B.17)] together by $\partial_t = \partial_{t_0} + \epsilon\partial_{t_1}$ and recalling that $\epsilon = \delta_t$, we have the Navier-Stokes equations [accurate up to the order of $O(M^2)$ in momentum equation]:

$$\partial_t \rho + \nabla\cdot(\rho \boldsymbol{u}) = 0\,, \tag{B.19a}$$

$$\partial_t \boldsymbol{u} + \boldsymbol{u}\cdot\nabla \boldsymbol{u} = -\frac{1}{\rho}\nabla P + \nu\nabla^2\boldsymbol{u} + \boldsymbol{a}\,, \tag{B.19b}$$

where the viscosity is given by

$$\nu = (\frac{\tau}{g} - \frac{1}{2})\,\theta\,\delta_t = \frac{(2\tau - g)}{6g}\frac{\delta_x^2}{\delta_t}\,,$$

and the pressure (the equation of state) is given by

$$P = \rho\,\theta\,(1 + b\rho\,g) = \frac{1}{3}c^2\,\rho\,(1 + b\rho\,g)\,, \tag{B.20}$$

where $\theta = c^2/3$ has been substituted. With the above equation of state, the sound speed, c_s, is given by

$$c_s^2 = \theta\left[1 + \frac{d}{d\rho}(b\rho^2\,g)\right] = \frac{1}{3}c^2\,\left[1 + \frac{d}{d\rho}(b\rho^2\,g)\right]\,. \tag{B.21}$$

It should be pointed out that, if instead of Eq. (B.8c), the following constraint is imposed:

$$\sum_\alpha \boldsymbol{e}_{\alpha,i}\boldsymbol{e}_{\alpha,j}F_\alpha = 0\,, \tag{B.22}$$

then, the term $\rho\boldsymbol{a}\cdot\boldsymbol{u}$, which is the work done by the force, does not appear in the energy balance equation. Therefore, the constraint of Eq. (B.8c) must be imposed to assure a correct energy balance equation.

Appendix C. Equilibrium Distribution Function Shifted by Acceleration.

If we start with the BGK Boltzmann equation without a forcing term:

$$\partial_t f + \boldsymbol{\xi}\cdot\nabla f = -\frac{1}{\tau\delta_t}[f - f^{(0)}]\,, \tag{C.1}$$

and assume that particle is impulsively accelerated by acceleration $\boldsymbol{a}$ with the mean free time $\tau\delta_t$. Under this circumstance, the equilibrium distribution function becomes [66]:

$$f^{(0)}(\rho,\,\boldsymbol{u} - \boldsymbol{a}\tau\delta_t,\,\theta) = \rho\,(2\pi\theta)^{-D/2}\,\exp\left[-(\boldsymbol{\xi} - \boldsymbol{u} + \boldsymbol{a}\tau\delta_t)^2/2\theta\right]\,. \tag{C.2}$$

Accordingly,

$$\begin{aligned} f^{(\mathrm{eq})} &= \rho\,(2\pi\theta)^{-D/2}\exp(-\boldsymbol{\xi}^2/2\theta)\times\left\{1 + \frac{\boldsymbol{\xi}\cdot(\boldsymbol{u} - \boldsymbol{a}\tau\delta_t)}{\theta} + \frac{[\boldsymbol{\xi}\cdot(\boldsymbol{u} - \boldsymbol{a}\tau\delta_t)]^2}{2\theta^2} - \frac{(\boldsymbol{u} - \boldsymbol{a}\tau\delta_t)^2}{2\theta}\right\} \\ &= \rho\,\omega(\boldsymbol{\xi})\,\left\{1 + \frac{\boldsymbol{\xi}\cdot\boldsymbol{u}}{\theta} + \frac{(\boldsymbol{\xi}\cdot\boldsymbol{u})^2}{2\theta^2} - \frac{\boldsymbol{u}^2}{2\theta}\left[\frac{m}{\theta}(\boldsymbol{\xi} - \boldsymbol{u}) + \frac{m^2\,(\boldsymbol{\xi}\cdot\boldsymbol{u})}{\theta^2}\boldsymbol{\xi}\right]\cdot\boldsymbol{a}\,\tau\delta_t\right\}\,. \end{aligned} \tag{C.3}$$

Here we have consistently ignored the terms of the order $O(\delta_t^2)$ or higher order. Substituting $\theta = c^2/3$, where $c \equiv \delta_x/\delta_t$, we have

$$f_\alpha^{(\mathrm{eq})} = w_\alpha\,\rho\,\left[1 + \frac{3(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})}{c^2} + \frac{9(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})^2}{2c^4} - \frac{3\boldsymbol{u}^2}{2c^2}\right] - 3\,w_\alpha\,\rho\,\tau\delta_t\left[\frac{1}{c^2}(\boldsymbol{e}_\alpha - \boldsymbol{u}) + \frac{3(\boldsymbol{e}_\alpha\cdot\boldsymbol{u})}{c^4}\,\boldsymbol{e}_\alpha\right]\cdot\boldsymbol{a}\,. \tag{C.4}$$

The second part of $f_\alpha^{(\mathrm{eq})}$ exactly produces the forcing term F_α obtained previously when $f_\alpha^{(\mathrm{eq})}$ is substituted into the following lattice Boltzmann equation without a forcing term:

$$f_\alpha(\boldsymbol{x} + \boldsymbol{e}_\alpha\delta_t,\,t + \delta_t) - f_\alpha(\boldsymbol{x},\,t) = -\frac{1}{\tau}\left[f_\alpha(\boldsymbol{x},\,t) - f_\alpha^{(\mathrm{eq})}(\boldsymbol{x},\,t)\right]\,. \tag{C.5}$$

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In this paper a procedure for systematic *a priori* derivation of the lattice Boltzmann models for non-ideal gases from the Enskog equation (the modified Boltzmann equation for dense gases) is presented. This treatment provides a unified theory of lattice Boltzmann models for non-ideal gases. The lattice Boltzmann equation is systematically obtained by discretizing the Enskog equation in phase space and time. The lattice Boltzmann model derived in this paper is thermodynamically consistent up to the order of discretization error. Existing lattice Boltzmann models for non-ideal gases are analyzed and compared in detail. Evaluation of these models are made in light of the general procedure to construct the lattice Boltzmann model for non-ideal gases presented in this work.

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